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Abstract

PROBLEM TO BE SOLVED: To provide an acrylic polymer having surely polymerizable unsaturated end groups and no well-known initiator end groups such as solvent residues, an azo compound or a peroxide and also containing neither an emulsifier nor a dispersing agent.

SOLUTION: The acrylic polymer having the polymerizable unsaturated group at the end of the molecule is obtained by reacting compounds (a)-(c). (a) an acrylic prepolymer whose number average molecular weight is 500-100,000 by GPC is made by blockpolymerizing a polymerizable monomer which makes a (meta)alkylacrylic ester the main components, in the presence of the inert gas atmosphere by applying the compound having a thiol group and a hydroxyl group in the molecule as an initiator, (b) an isocyanate compound having two or more isocyanate group in the molecule and (c) a compound having a hydroxyl and the polymerizable unsaturated group in the molecule.

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(54)[TITLE of the Invention] An acrylic polymer which has a polymerizable unsaturated group at the molecule terminal

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(57)[ABSTRACT of the Disclosure]
[SUBJECT of the Invention] It is a polymerizable unsaturated group's being reliably transduced into the molecule terminal, and providing the acrylic polymer which does not have conventionally well-known initiator residues, such as a solvent compound residue, and an azo group, a peroxide group, in the molecule terminal excluding an emulsifier or a dispersing agent.

[PROBLEM to be solved] The acrylic polymer which has a polymerizable unsaturated group at the molecule terminal makes the following compound (a) - (c) react, and is obtained.
(a) Coming to carry out block polymerization of the polymerizable monomer

which has the meth acrylic acid alkylester as a main component to inert-gas atmosphere using the compound which has a thiol group and a hydroxyl group in the molecule as a polymerization initiator, it is the acrylic prepolymer which is the number average molecular weight 500-100,000 by GPC, (b) It is the isocyanate compound which has two or more isocyanate groups in the molecule, (c) It is the compound which has a hydroxyl group and a polymerizable unsaturated group in the molecule.

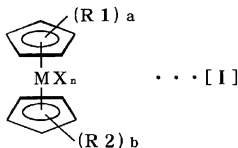
[CLAIMS]

[CLAIM 1] An acrylic polymer wherein in the acrylic polymer to which the component of following (a)-(c) is made to come to react, (a) coming to carry out block polymerization of the polymerizable monomer which has the (meth)acrylic acid alkylester as a main component to inert-gas atmosphere using the compound which has a thiol group and a hydroxyl group in the molecule as a polymerization initiator, it is the acrylic prepolymer which is the number average molecular weight 500-100,000 by GPC, (b) it is the isocyanate compound which has two or more isocyanate groups in the molecule, (c) it is a compound which has a hydroxyl group and a polymerizable unsaturated group in the molecule, and having an acrylic polymer having a polymerizable unsaturated group at the molecule terminal.

[CLAIM 2] The acrylic polymer of Claim 1 wherein the number-of-moles of the isocyanate group of said compound (b) are 100 - 120 mol to a total of 100 mol of the number-of-moles of the hydroxyl group of said compound (a), and the number-of-moles of the hydroxyl group of said compound (c).

[CLAIM 3] Said block polymerization is the metallic compound expressed with the following (I) type, comprising:

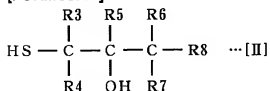
[FORMULA 1]



An acrylic polymer of Claim 1 or 2 wherein, in the above-mentioned (I) formula, m is a metal chosen from the group consisting of the periodic table 4A group, 4B group, 5A group, 5B group's metal, chrome, ruthenium, and palladium, r1 and R2, each independently, are at least 1 type of group, hydrogen atom or single bond chosen from the group comprising a certain aliphatic hydrocarbon having had a substituent, a certain alicyclic hydrocarbon group having had a substituent, a certain aromatic hydrocarbon group having had a substituent, and a certain silicon containing group having had a substituent, and furthermore, two five-membered rings in the compound by which R1 and R2 are jointly expressed with said Formula (I) may be connected, and two or more adjoining R1 or R2 may form the cyclic structure jointly, and a and b are the integers of 1-5 independently, respectively, and X is also a certain hydrocarbon group or a halogen atom wherein at least one part of a hydrogen atom is replaced by the halogen atom, n is the integer of the valence -2 of 0 or Metal M, and it is used as a catalyst of a polymerization initiator.

[CLAIM 4] Said polymerization initiator is expressed with a following (II) type.

[FORMULA 2]



The acrylic polymer of any of Claim 1-3 wherein, in the above-mentioned (II)

type, R3-R7 are each a hydrogen atom or a C1-C12 alkyl group independently, and R8 is at least 1 group chosen from the group comprising a hydroxyl group, a C1-C12 alkoxy group, and a C1-C12 alkyl group.

[DETAILED DESCRIPTION of the INVENTION]**[0001]**

[TECHNICAL FIELD of the Invention] This invention relates to the acrylic polymer which has a polymerizable unsaturated group at the molecule terminal useful for coating material, adhesive, and casting material etc.

[0002]

[PRIOR ART] The oligomer or polymer which has a polymerizable unsaturated group at the molecule terminal of the polymer obtained by polymerizing a monomer is called a macro monomer, and it is utilized widely for a coating material, an adhesive, casting material, etc.

Ionic polymerization and radical polymerization are known as a manufacturing method of this macro monomer.

However, when the composition of the principal chain of a macro monomer has an acrylic monomer as a main component, after preparing the prepolymer which has a functional group at the terminal by radical polymerization usually, the compound which has the functional group and reactivity is made to react, and it manufactures.

[0003] More specifically, it polymerizes using a mercaptoacetic acid as an acrylic monomer and azo group initiator or a peroxide group initiator, and a chain transfer agent, and the prepolymer which has a carboxyl group at the molecule terminal is prepared, it polymerizes using a mercaptoethanol as the method to which the carboxyl group and glycidylmethacrylate are made to react, an acrylic monomer and azo group initiator or a peroxide group initiator, and a chain transfer agent, and the prepolymer which has a hydroxyl group at the molecule terminal is prepared, and there is a method to which the hydroxyl group and 2-isocyanate ethylmethacrylate are made to react.

[0004] The method of preparing a prepolymer by making into a chain transfer agent the mercaptans which have these functional groups is usually performed

by solution polymerization, polymer molecular designs, such as a control of the polymerization reactions, such as a rate of polymerization and an exothermic control, and molecular weight, a molecular weight distribution, are performed by adjusting suitably the amount used or the kinds as the polymerization temperature, the radical polymerization start agent amount, and a radical chain transfer agent, such as an organic solvent and mercaptans.

It will have an unsaturated group at the time of residues, such as a compound used as a radical polymerization initiator or a compound used as a chain transfer agent, and a solvent compound at the time of carrying out a chain transfer, connecting the molecule terminal of the polymer obtained by this method, or carrying out a disproportionation termination.

In other words, a terminal group will not be able to control the polymer obtained sufficiently, but it will become the mixture of a polymer with various terminal groups.

[0005] For this reason, by the method of preparing these former prepolymers, the molecule into which the polymerizable unsaturated group is not introduced is obtained.

The molecule by which a polymerizable unsaturated group is not introduced as design will be obtained.

When such a macro monomer is used as raw materials, such as a coating material, an adhesive, and casting material, the physical property as design is not acquired in many cases.

[0006] Moreover, the water-based radical-polymerizing method of emulsification-polymerization and suspension polymerization is learned as a preparation method of a prepolymer.

However, in the case of emulsification-polymerization or suspension polymerization, the dissolution to the solvent for making the compound which has the precipitate for separating from the water which is a dispersion medium, filtration, washing, drying, and the functional group of a prepolymer and reactivity react etc. needs to be operated after polymerization of a prepolymer.

The process becomes complicated.

[0007] Furthermore, the aggregated-form polymerizing method is known as a

preparation method of a prepolymer.

Aggregated-form polymerizing method, since a solvent and a dispersion medium are not used and an impurity like the organic solvent which does not need to use the organic solvent, water, a dispersing agent, an emulsifier, etc., and participates in polymerization is not included, a reaction system not only becomes brief, but it becomes as follows.

In order for there to be no mixing of impurities, such as an emulsifier and a dispersing agent, into the polymer obtained and to obtain the target prepolymer further, elimination of a dispersion medium is also unnecessary.

[0008] However, in general, with an aggregated-form polymerizing method, the polymerization reaction rate is remarkably quick and actually it is very difficult to control this aggregated-form polymerizing method.

Moreover, the polymer generated by high temperature, without a rate of polymerization being uncontrollable changed into the state with the unstable terminal group of a molecule by disproportionation termination.

A low-molecular-weight object is formed, conversely, branch-izing and a gelling of a polymer tend to take place by hydrogen drawing out from the polymer which was being generated previously etc.

For this reason, molecular weight of a polymer, that molecular designs, such as a molecular weight distribution, become difficult, from the first, by generation of branch-izing of a polymer, the disproportionation-termination terminal, etc., design of clear molecular structure becomes difficult.

Furthermore, gelled material may generate rapidly and in large quantities.

In the worst case, it becomes impossible to restrict the temperature rise of a reaction material, and there is even danger of an explosion.

[0009] Among an acrylic monomer, since the methyl methacrylate has the property that a rate of polymerization is comparatively slow, a reaction control can be performed also according to a block polymerization, and, as for the controlling method, examination is made from old times, and in order to control molecular weight and a molecular weight distribution, the mercaptan is used as a chain transfer agent.

The polymerization start utilizes addition of an azo group polymerization initiator or a peroxide group polymerization initiator, or the heat start polymerization in high temperature.

For this reason, the compound derived from a polymerization initiator connects with the polymer terminal, or, in heat start polymerization, the polymer which the compound derived from the peroxide of a polymer monomer connected with the terminal comes to be contained at the polymer obtained by these reactions, and the strict control of the compound connected with the terminal cannot be performed.

[0010] Moreover, at the block-polymerization reaction using such a mercaptan, since the initiator remains in the reaction system even if the mercaptan consumption velocity under polymerization and the consumption velocity of an initiator do not constitute into a constant velocity but all mercaptans are consumed during polymerization, it is common for it to be difficult to control a reaction uniformly, and the monomer used for by block polymerization also has a limit.

[0011] The polymerization method, polymerization catalyst, and polymerization initiator for obtaining the polymer which controlled the terminal sufficiently from such a reason are needed.

[0012] Incidentally, a catalyst changes with monomers which use the polymerization reaction, for example, a metallocene compound like a titanocene as polymerization catalysts, such as ethylene, is used.

However, if it excludes using this metallocene compound with a sensitizer in photopolymerization, most things for which this metallocene compound is used as a polymerization catalyst of monomers other than a (alpha)-olefin are not known.

In the photopolymerization composition which contains in Unexamined-Japanese-Patent No. 9-5996 the sensitizer which can sensitize a titanocene compound and this titanocene compound as the compound which has at least 1 of the ethylenically unsaturated double bond which can carry out addition polymerization, and a photopolymerization start group, this composition, furthermore, invention of the photopolymerisable composition which is that which contains a heterocyclic thiol compound is indicated.

In the invention currently disclosed by this gazette, the titanocene compound is used as a photopolymerization catalyst.

There is no publication about using a titanocene compound as a catalyst of

block polymerization.

Moreover, the heterocyclic thiol compound indicated by this gazette is a visualization photosensitizer.

[0013] Generally, in a metallocene compound like a titanocene compound, a sulfur containing compound is a compound which reduces the catalysis of a metallocene compound.

It is a very exceptional method of application to use a sulfur containing compound as a compound which shows a specific effect as mentioned above like a visualization photosensitizer on the occasion of use of the metallocene compound as a catalyst.

That is, generally a sulfur containing compound is a compound which serves as a catalyst poison to the metallocene compound as a catalyst.

Therefore, it is made not desirable for the reaction system which considers a metallocene compound as a catalyst to add a sulfur compound.

[0014]

[PROBLEM to be solved by the Invention] The subject of this invention is there being no conventionally well-known initiator residues, such as a solvent compound residue, and an azo group, a peroxide group, in the molecule terminal, and providing the acrylic polymer whose molecule terminal's is a polymerizable unsaturated group reliably excluding an emulsifier or a dispersing agent.

[0015]

[MEANS to solve the Problem] The acrylic polymer which has the polymerizable unsaturated group of this invention at the molecule terminal, the acrylic prepolymer obtained by a block polymerization using the compound which has a thiol group and a hydroxyl group in the molecule as a polymerization initiator, the isocyanate compound which has two or more isocyanate groups in the molecule, and the compound which has a hydroxyl group and a polymerizable unsaturated group in the molecule are used, and it is obtained by making them react.

However, it is when preparing an acrylic prepolymer, the compound which has a thiol group and a hydroxyl group in the molecule as a polymerization initiator is used, without it has an initiator residue originating in a conventionally well-

known azo group initiator or a peroxide form initiator at the molecule terminal of the polymer obtained, since it is a block polymerization in nitrogen atmosphere, a polymer color, the solvent compound residue in solution polymerization is not introduced into the molecule terminal excluding the emulsifier or dispersing agent in emulsification-polymerization and suspension polymerization.

[0016]

[EMBODIMENT of the Invention] It has a polymerizable unsaturated group at the molecule terminal by this invention below.

Embodiment of the acrylic polymer characterized by the above-mentioned is demonstrated.

This acrylic polymer by this invention, (a) Coming to carry out block polymerization of the polymerizable monomer which has the (meth)acrylic acid alkylester as a main component to inert-gas atmosphere using the compound which has a thiol group and a hydroxyl group in the molecule as a polymerization initiator, the acrylic prepolymer which is the number average molecular weight 500-100,000 by GPC

(b) The isocyanate compound which has two or more isocyanate groups in the molecule

(c) The compound which has a hydroxyl group and a polymerizable unsaturated group in the molecule

These are made to react and it is obtained.

[0017] The acrylic prepolymer of said (a) carries out block polymerization of the polymerizable monomer which has the (meth)acrylic acid alkylester as a main component using the compound which has a thiol group and a hydroxyl group in the molecule as a polymerization initiator to inert-gas atmosphere, and is obtained.

[0018] The compound used for the initiator of this block polymerization has the thiol group and the hydroxyl group in the molecule.

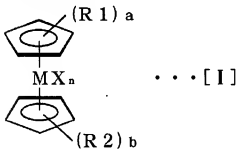
Specifically, mercapto methanol, 1-mercaptoethanol, 1-mercapto propanol, 1-mercapto- 2,3- propanediol, 1-mercapto- 2-butanol, 1-mercapto- 2,3-butanediol, 1-mercapto- 3,4- butanediol, the 1-mercapto- 3,4,4'-butane triol, a 2-mercapto- 3-butanol, 2-mercapto- 3,4- butanediol, the 2-mercapto- 3,4,4'-

butane triol, etc. can be mentioned.

[0019] Said compound which has a thiol group and a hydroxyl group in the molecule is 0.01 - 100 mol to 100 mol of acrylic monomers mentioned later, preferably, 0.1 - 50 mol adds.

[0020] Moreover, in order to gather the polymerization efficiency of initiator of a compound which is said polymerization initiator and which has a thiol group and a hydroxyl group in the molecule, it is desirable to add the organometallic compound expressed with following Formula (I) to a polymerization system. Said organometallic compound acts as a decomposition catalyst of a compound which is a polymerization initiator and which has a thiol group and a hydroxyl group in the molecule.

[FORMULA 3]



However, in said Formula (I), m is a metal chosen from the group which is made of metals from periodic table 4A group, 4B group, 5A group, 5B group, chrome, ruthenium, and palladium.

Specifically, m is titanium, zirconium, chrome, ruthenium, vanadium, palladium, tin, etc.

Moreover, in formula (I), r1 and R2, each independently, is at least 1 type of group chosen from a group consisting of

An aliphatic hydrocarbon having had a substituent, an alicyclic hydrocarbon having had a substituent, an aromatic hydrocarbon group having had a substituent, and a silicon containing group having had a substituent.

It is in a gap of a hydrogen atom or a single bond.

Further, r1 and R2 may connect this two five-membered ring jointly, moreover, two or more adjoining R1 or R2 may form the cyclic structure jointly.

Moreover, in formula(I), and b is the integer of 1-4 independently, respectively. As for X, also a certain hydrocarbon group that at least one part of halogen atoms, such as chlorine, a bromine, and an iodine, or a hydrogen atom is replaced by the halogen atom.

N is 0 or the integer of the valence -2 of Metal M.

As an example of such an organometallic compound, dicyclopentadiene-Ti-dichloride, dicyclopentadiene-Ti-bis phenyl, dicyclopentadiene-Ti-bis- 2, 3,4,5,6-Pentafluorophenyl-1- yl, dicyclopentadiene-Ti-bis- 2,3,5,6-Tetrafluoro phenyl -1- yl, dicyclopentadiene-Ti-bis- 2,5,6-Trifluoro phenyl -1- yl, dicyclopentadiene-Ti-bis- 2,6- Difluoro phenyl -1- yl, dicyclopentadiene-Ti-bis- 2,4- Difluoro phenyl -1- yl, dimethyl cyclopentadienyl-Ti-bis- 2, 3,4,5,6-pentafluoro phenyl -1- yl, dimethyl cyclopentadienyl-Ti-bis- 2,3,5,6-tetrafluoro phenyl -1- yl, a titanocene compound like a dimethyl cyclopentadienyl-Ti-bis- 2,6- difluoro phenyl -1- yl and a dimethyl cyclopentadienyl-Ti-bis- 2,6- difluoro -3-(pyl-1- yl)-phenyl -1- yl; A zirconocene compound like a dicyclopentadienyl-Zr-dichloride and a dimethyl cyclopentadienyl-Zr-dichloride;

A ruthenocene compound, a black ore compound, etc. can be mentioned.

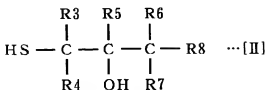
These organometallic compounds can be used separately or in combination.

[0021] This organometallic compound is usually 1.0 - 0.00001 mol to said compound 100 mole which has a thiol group and a hydroxyl group in the molecule, preferably it is used by the 0.1 - 0.0001-mol amount.

A manufacturing cost becomes higher and is not preferable, if it is less than 0.00001 mol, and the effect as a catalyst with respect to a compound which has the thiol group and hydroxyl group which are an initiator is low and exceeds 1.0 mol.

[0022] Furthermore, the independent polymerization initiator ability of the compound expressed with following Formula (II) whose hydroxyl group is a secondary hydroxyl group in said compound which has the thiol group and the hydroxyl group in the molecule is highly preferable.

[FORMULA 4]



However, in said Formula (II), r3-R7 are each independently a hydrogen atom or a C1-C12 alkyl group, r8 is at least 1 group chosen from the group which consists of a hydroxyl group, a C1-C12 alkoxy group, and a C1-C12 alkyl group.

[0023] The acrylic monomer used in order to prepare the acrylic prepolymer of said (a) is having the (meth)acrylic acid alkylester as a main component.

(Meta)

As an example of an alkyl acrylate ester, a methyl (meth)acrylate, an ethyl (meth)acrylate, the (meth)acrylic acid propyl, a butyl (meth)acrylate, the (meth)acrylic acid pentyl, the (meth)acrylic acid hexyl, the (meth)acrylic acid -2-ethylhexyl, the (meth)acrylic acid octyl, the (meth)acrylic acid nonyl, the (meth)acrylic acid decyl, the (meth)acrylic acid dodecyl, etc. are mentioned.

[0024] The acrylic monomer used by this invention may combine a 2 type or more types of monomer, although the monomer of the 1 type of the (meth)acrylic acid alkylester is also good.

Furthermore, the monomer which may combine monomers other than the (meth)acrylic acid alkylester, for example, is shown below can be mentioned.

(Meta)

Salts, such as acrylic acid and the (meth)acrylic acid alkali metal salt;

The (meth)acrylic acid phenyl, (meth)acrylic acid aryl ester like the (meth)acrylic acid benzyl;

The (meth)acrylic acid methoxy ethyl, the (meth)acrylic acid ethoxyethyl, the (meth)acrylic acid propoxy ethyl, the (meth)acrylic acid butoxy ethyl, a (meth)acrylic acid alkoxy alkyl like the (meth)acrylic acid ethoxy propyl;

The di(meth)acrylic-acid ester of an ethylene glycol, the di(meth)acrylic-acid ester of diethylene glycol, the di(meth)acrylic-acid ester of a triethyleneglycol, the di(meth)acrylic-acid ester of polyethyleneglycol, the di(meth)acrylic-acid SL of a propylene glycol, the di(meth)acrylic-acid SL of a dipropylene glycol, di(meth)acrylic-acid ester of alkylene glycol like the di(meth)acrylic-acid ester

(poly) of a tri propylene glycol;

(meth)acrylonitrile;

Vinyl acetate;

Vinyl chloride;

Vinylidene chloride;

A halogenated vinyl compound like the (meth)acrylic acid -2- chloroethyl;

(meth)acrylic ester of alicyclic alcohol like the (meth)acrylic acid cyclohexyl;

An oxazoline group containing polymerizable compound like 2-vinyl -2-oxazoline, 2-vinyl -5- methyl -2- oxazoline, and 2-isopropenyl -2- oxazoline;

An aziridine group containing polymerizable compound like (meth)acryloyl aziridine and the (meth)acrylic acid -2- aziridiny ethyl;

An epoxy-group containing vinyl monomer like an arylglycidyl ether, the (meth)acrylic acid glycidyl ether, and the (meth)acrylic acid -2- ethyl glycidyl ether;

A hydroxyl-group containing vinyl compound like a monoester with the (meth)acrylic acid -2- hydroxyethyl, the (meth)acrylic acid -3- hydroxy propyl, (meth)acrylic acid -2- hydroxy propyl, (meth)acrylic acid -4- hydroxy butyl, (meth)acrylic acid polypropylene glycol, or polyethyleneglycol, and an addition product with lactone and the (meth)acrylic acid -2- hydroxyethyl;

Fluorine-containing vinyl monomers, such as a fluorine displacement (meth)acrylic acid alkylester;

Itaconic acids, crotonic acids, maleic acid and unsaturated carboxylic acids like a fumaric acid except (meth)acrylic acid, these salts, these (part) ester compounds, and acid anhydride;

2-chloro ethyl vinyl ether, reactive halogen containing vinyl monomer like monochloro vinyl acetate;

Amide-group containing vinyl monomer like (meth)acrylamide, N-methylol (meth)acrylamide, N-methoxy ethyl (meth)acrylamide, and N-butoxy methyl (meth)acrylamide;

Vinyl trimethoxysilane, (gamma)- methacryloxy propyl trimethoxysilane, allyl trimethoxysilane, trimethoxy silylpropyl allylamine, organic silicon group containing vinyl-compound monomer like 2-methoxy ethoxy trimethoxysilane;

And a diene compound like ethylidenenorbornene, piperidine, isoprene, pentadiene, vinyl cyclohexene, chloroprene, butadiene, methyl butadiene, cyclobutadiene, and methyl butadiene.

These are mentioned.

[0025] Furthermore, it is good also as a polymer of the multi-branch structure combining monomers which have two or more polymerizable unsaturated groups in the molecule, such as a multivalent (meth)acrylic ester like a trimethylol-propane tri (meth)acrylic ester, divinylbenzene, an ethylene glycoldi(meth)acrylate, a neopentyl glycoldi(meth)acrylate, a dimethylol tricyclo decan di (meth)acrylate, and 2,2-bis (4-(meta) (acryloxy ethoxy) phenyl) propane.

[0026] The acrylic prepolymer of said (a) uses for inert-gas atmosphere said compound which has a thiol group and a hydroxyl group in the molecule as a polymerization initiator, carries out block polymerization of the polymerizable monomer which has said (meth)acrylic acid alkylester as a main component, and is obtained.

However, it is necessary to be the number average molecular weight 500-100,000 by GPC.

It is preferable that it is 500-10,000.

When the content of the acryl skeleton contained in one molecule as a number average molecular weight is less than 500 is low, and character peculiar to a (meth)acryl skeleton does not express but it is made to react with said compound (b), a precipitate phenomenon is caused for crystalline increase.

Moreover, after making it react with said compound (b), when making it react with said compound (c), it is easy to cause decline in a reaction rate for the precipitate phenomenon.

Furthermore, when a number average molecular weight exceeds 100,000, when it is a reaction with said compound (b) and said compound (c), by increase of viscosity and decrease of fluid, etc.

While operativity deteriorates, it is easy to cause decrease in a reaction rate.

[0027] The isocyanate compound which has two or more isocyanate groups in the intramolecular of said (b) used by this invention

Specifically tolylene diisocyanate (TDI), tolylene diisocyanate, lysine triisocyanate, chloro phenylene diisocyanate, diisocyanate diphenylmethane, hexamethylene diisocyanate, tetramethylene diisocyanate, isocyanate monomers, such as an isophorone diisocyanate and a diphenylmethane diisocyanate which was hydrogenated, and the isocyanate compound and the

isocyanurate formation thing which added these isocyanates monomer with the trimethylol propane etc., a buret type compound, urethane-prepolymer type isocyanates which carried out the addition reaction, such as still well-known polyether polyol and polyester polyol, acryl polyol, polybutadiene polyol, and polyisoprene polyol, can be mentioned. It is preferable to use the compound which has two to three isocyanate groups as an isocyanate compound used particularly for this invention.

[0028] As a polymerizable unsaturated group of a compound which has a hydroxyl group and a polymerizable unsaturated group in said (c) intramolecular used by this invention, they are a (meth)acryloyl group, a vinyl group, an aryl group, etc.

As a concrete compound, 2-hydroxyethyl (meth)acrylate, 3-hydroxy-propyl (meth)acrylate, 4-hydroxy butyl (meth)acrylate, vinyl alcohol, allyl alcohol, etc. are mentioned.

[0029] For the isocyanate compound which has two or more isocyanate groups in the (b) intramolecular used by this invention, an isocyanate group is usually 100 - 120 mol to the hydroxyl group which exists in the acrylic prepolymer in the acrylic prepolymer of said (a), and 100 mol of hydroxyl groups of the compound which has a hydroxyl group and a polymerizable unsaturated group in said (c) intramolecular, it is used by amount which preferably becomes 105 - 115 mol.

[0030] The reaction of the isocyanate compound which has two or more isocyanate groups in the acrylic prepolymer of said (a) and said (b) intramolecular, and the compound which has a hydroxyl group and a polymerizable unsaturated group in said (c) intramolecular makes the isocyanate compound which has two or more isocyanate groups react to the acrylic prepolymer and said (b) intramolecular of said (a).

After preparing the prepolymer which has an isocyanate group at the molecule terminal, the compound which has a hydroxyl group and a polymerizable unsaturated group in said (c) intramolecular may be made to react to the prepolymer, and the isocyanate compound which has two or more isocyanate groups in said (b) intramolecular, and the compound which has a hydroxyl group and a polymerizable unsaturated group in said (c) intramolecular are made to react.

After preparing the compound which has an isocyanate group and a polymerizable unsaturated compound, it may make the acrylic prepolymer of said (a) react.

[0031] The acrylic polymer which has a polymerizable unsaturated group at the molecule terminal of this invention is a liquid with this viscous polymer.

From having a polymerizable unsaturated group, for example, the coated coating resin and a sheet formed product on the surface of an inorganic material such as an adhesive, an adhesive, a vehicle for coating materials, a resin for primers, a binder for ink, a cement and mortar, a metal, glass, etc., (Example; air-permeable-sheet, protection sheet, water-barrier sheet, damping sheet, transfer-sheet, modulated-light sheet, antistatic sheet, electroconductive sheet, and curing sheet, sound-insulation sheet, shading sheet, decorative-sheet, marking sheet, and flame retardant sheet), film formed product (Example; Marking film, protective-film, ink fixing film, and laminate-film) Foam (hard foam, soft foam, semi-hard foam, flame retardant foam, etc. are included).

As a binder and a reactive diluent for a reaction plasticizer, a plasticizer, a diluent, a solubilizer, and UV curable resins, the resin binder for radical hardening sirup type traffic paints and a diluent, and an intermediary raw material, raw materials for resins, such as a raw material for denaturants for rubber, such as the grafting agent at the time of the vinyl-based resin synthesis, a block agent, and NBR, IIR, SBR, and a crosslinker, and modifiers, and various block polymers as a macromer, or the raw material for modification, an additive. Furthermore, it can be utilized for a fiber modifier, a fiber surface treating agent, a paper process agent, a paper modifier, a surfactant, a dispersion stabilizer, a dispersion medium, a solvent, a viscosity regulator, an absorbent, a hair-treatment agent, an additive for toners, an electrical charging controlling agent, an antistatic agent, a low contraction agent, an anti-fog agent, a stain proofing agent, a hydrophilic providing agent, a lipophilic providing agent, a pharmaceutical carrier, a carrier for agrochemicals, a compounding agent for cosmetics, a lubricating agent, an additive for polymer alloys, the gel-coating agent, the resin for FRP, additive for FRP resins, resin for artificial marbles, resin additive for artificial marbles, resin for the implantation molded products, and raw material for a UV*EV cured resin, a tackifier, various binders (For example; the binder for magnetic recording media, the binder for casting,

the binder for baked objects, binder for glass fiber sizing materials)

Urethane modifier for RIM, resin for glass laminates, a vibration damper, an insulator material, the resin for separation membranes, a sound insulating material, a sound absorbing material, an artificial leather, artificial skin, a synthetic leather, various industrial components, daily necessities, the molded product for toiletries, a binder for resist materials, an additive for resist materials, a diluent for resist materials, a resist agent, an additive for photoresist materials, a diluent, a binder, others, a release regulator etc.

[0032]

[EXAMPLES] Below, an Example further demonstrates this invention in detail. However, this invention is not limited by these Examples.

[0033] Manufacture of an acrylic prepolymer

[MANUFACTURE 1] The contents of a flask were heated at 80 degrees C, having prepared 90 weight-parts of butylacrylates, 10 weight-parts of 2-hydroxymethyl methacrylate, and 0.1 weight-parts of ruthenocene dichlorides in the flask equipped with the stirring apparatus, the nitrogen introducing pipe, the thermometer, and the reflux cooling pipe, and transducing nitrogen gas into it in a flask.

[0034] Subsequently, 10 weight-parts of 2-mercaptoethanols which fully carried out nitrogen gas displacement were added in the flask while stirring.

Heating and cooling were performed for 4 hours so that the temperature of the contents in a flask could be maintained at 80 degrees C.

Furthermore, it reacted for 4 hours, further performing heating and cooling so that the temperature of the contents in a flask can maintain at 90 degrees C, after carrying out additional addition of the 10 weight-parts of the 2-mercaptoethanols which fully carried out nitrogen gas displacement into the flask under churning.

[0035] One part of a reaction material is collected after the above-mentioned reaction, a benzoquinone solution (95-% THF solution) is added, the polymerization degree was 78 % when the monomer residual rate was

measured using the gas chromatography.

[0036] After adding 0.1 weight-parts of benzoyl peroxides to the reaction material continued and obtained as a radical polymerization initiator and making it polymerize a unreacted monomer, a reaction material is moved to an evaporator, and the residual monomer and the residual initiator were removed heating gradually to 80 degrees C to under reduced pressure.

[0037] In this way, 150-degree-C heating residue of obtained acrylic prepolymer (A) was 96.3 %.

Moreover, the molecular weight measured by the gel permeation chromatography (GPC) about obtained acrylic prepolymer (A) is $M_w=950$, $M_n=650$, and distributed index = 1.5.

The viscosity in 23 degrees C was 0.85 (Pa*s).

[0038]

[MANUFACTURE 2] Nitrogen gas replaced the air of a flask, having prepared 100 weight-parts of butylacrylates in the flask equipped with the stirring apparatus, the nitrogen gas introducing pipe, the thermometer, and the reflux cooling pipe, and transducing nitrogen gas into it in a flask.

Furthermore, the contents of a flask were heated at 60 degrees C, transducing nitrogen gas.

[0039] Subsequently, 6 weight-parts of 1-mercapto- 2,3- propanediol which fully carried out nitrogen gas displacement were added in the flask under churning as a polymerization initiator.

Heating and cooling were performed for 4 hours so that the temperature of the contents in a flask could maintain at 60 degrees C.

[0040] One part of a reaction material is collected after the above-mentioned reaction, a benzoquinone solution (95-% THF solution) is added, the polymerization degree was 75 % when the monomer residual rate was measured using the gas chromatography.

Next, the obtained reaction material is moved to an evaporator, the residual monomer and the residual initiator were removed heating gradually to 80 degrees C to under reduced pressure.

[0041] In this way, 150-degree-C heating residue of obtained acrylic prepolymer (B) was 99.6 %.

Moreover, the molecular weight measured by gel permeation chromatography (GPC) about obtained acrylic prepolymer (B) is $M_w=3400$, $M_n=1700$, and distributed index ≈ 2.0 .

The viscosity in 23 degrees C was 2.6 (Pa*s).

[0042]

[Comparison manufacture example 1] The contents of a flask were heated at 80 degrees C, having prepared 90 weight-parts of butylacrylates, and 10 weight-parts of 2-hydroxymethyl methacrylate in the flask equipped with the stirring apparatus, the nitrogen gas introducing pipe, the thermometer, and the reflux cooling pipe, and transducing nitrogen gas into it in a flask.

[0043] Subsequently, 18 weight-parts of 2-mercaptoethanols are added while stirring, it continued, and it added gradually as a radical polymerization initiator, having applied 2 weight-parts of 2-mercaptoethanols and 0.1 weight-parts of azobisisobutyronitrile in the flask for 1 hour.

After adding this, it reacted for 7 hours, performing cooling and a heating so that the temperature of the contents in a flask can maintain at 80 degrees C.

[0044] After performing the above-mentioned reaction for a total of 8 hours, one part of a reaction material is collected, a benzoquinone solution (95-% THF solution) is added, and the polymerization degree was 87 % when the monomer residual rate was measured using the gas chromatography.

Next, the obtained reaction material is moved to an evaporator, the residual monomer and the residual initiator were removed heating gradually to 80 degrees C to under reduced pressure.

[0045] In this way, 150-degree-C heating residue of the obtained acrylic prepolymer (C-1) was 96.3 %.

Moreover, the molecular weight measured by GPC about the acrylic prepolymer (C-1) is $M_w=930$, $M_n=610$, and distributed index ≈ 1.5 .

The viscosity in 23 degrees C was 0.80 (Pa*s).

[0046]**[EXAMPLE 1]**

In the flask equipped with the reflux cooling pipe which equipped a stirring apparatus, a dry-nitrogen gas introducing pipe, a thermometer, a dropping funnel, and a molecular sieve, 49 weight-parts of hexamethylene diisocyanates and 50 weight-parts of toluene were prepared as an isocyanate compound, and while dry-nitrogen gas replaced the air in a flask, it heated to 60.

After that, to maintain within the limits of temperature of 60 - 70 degrees C in a flask, while performing heating and cooling, the mixture was added dropwise in the flask over 2 hours with 0.1 weight-parts of dibutyl tin dilaurates and 100 weight-parts of acrylic prepolymer (A) obtained by the manufacture example 1.

The reaction was further performed for 2 hours, performing cooling and a heating after completion of dripping, so that the temperature in a flask can be maintained at 70 degrees C.

[0047] After that, what dissolved 0.001 weight-parts of mono-ethyl hydroquinone in 42 weight-parts of 2-hydroxyethyl acrylates was added dropwise at the flask over 1 hour.

After completion of dripping, the reaction was performed at 70 degrees C as it was for 2 hours.

After that, it cools to room temperature, and the reaction material in a flask was moved to the evaporator.

By the evaporator, toluene, a unreacted isocyanate compound, and a unreacted monomer are removed, heating gradually to 80 degrees C to under reduced pressure, and the acrylic polymer (1) which has a polymerizable unsaturated group at the molecule terminal was obtained.

[0048] Of the acrylic polymer (1) which has obtained polymerizable unsaturated group at the molecule terminal, the heating residue at 150 degrees C is 99.8 %.

The viscosity in 23 degrees C was 48 (Pa*s).

In this way, when the obtained acrylic polymer (1) is investigated by FT-IR (Fourier-transformation infrared absorption spectrum), absorption resulting from a hydroxyl group is lost completely, the acryloyl group originating in 2-hydroxyethyl acrylate was observed.

[0049]

[EXAMPLE 2] Acrylic prepolymer (B) obtained manufacture-example 2 instead of acrylic prepolymer (A) is used, and it is made to be the same as that of Example 1 except having made 49 weight-parts of hexamethylene diisocyanates into 18.5 weight-parts, the acrylic polymer (2) which has a polymerizable unsaturated group at the molecule terminal was obtained.

[0050] Of the acrylic polymer which has the obtained polymerizable unsaturated group at the molecule terminal (2), the heating residue at 150 degrees C is 99.7 %.

The viscosity in 23 degrees C was 84 (Pa*s).

In this way, when the obtained acrylic polymer (2) is investigated by FT-IR (Fourier-transformation infrared absorption spectrum), absorption resulting from a hydroxyl group is lost completely, the acryloyl group originating in 2-hydroxyethyl acrylate was observed.

[0051]

[COMPARATIVE EXAMPLE 1] It is made to be the same as that of Example 1 except having used the acrylic prepolymer (C-1) obtained comparison manufacture-example 1 instead of acrylic prepolymer (A), the acrylic polymer (3) which has a polymerizable unsaturated group at the molecule terminal was obtained.

[0052] The acrylic polymer (3) which has the obtained polymerizable unsaturated group molecule terminal, the heating residue at 150 degrees C is 99.4 %.

The viscosity at 23 degrees C was 45 (Pa*s).

In this way, when the obtained acrylic polymer (3) is investigated by FT-IR (Fourier-transformation infrared absorption spectrum), absorption resulting from a hydroxyl group is lost completely, the acryloyl group originating in 2-hydroxyethyl acrylate was also observed.

[0053]

[REFERENCE 1] It is acrylic-type polymer (1) 100 weight-part to a beaker with a capacity of 200 ml, and as an initiator, 0.1 weight-parts of 1,1,3,3-tetramethyl butylperoxy -2- ethyl hexanoates (brand name: Perocta O, Nippon Oil & Fats

Co., Ltd. make) are mixed, it fully stir-mixed by the mixer until the contents in a beaker became uniform.

A burr coder is used for a polyethylene film (film thickness of 50 micrometer), and the obtained blend material is applied to 50 micrometer of paint cloth thicknesses, and the polyethylene film (film thickness of 50 micrometer) was put on it.

This is left for 60 minutes in 120-degree C drying machine.

The film compound (1) was obtained.

It was 82 %, when Soxhlet extraction which used the acetone solvent was performed and gel-fraction (%) was investigated about the obtained film compound (1).

[0054]

[REFERENCE 2] In Reference Example 1, it is made similar except having used the acrylic polymer (2), and film compound (2) was obtained.

It was 91 % when the gel fraction of the obtained film compound (2) was investigated.

[0055]

[Comparison Reference Example 1] In Reference Example 1, it is made similar except having used the acrylic polymer (3), and the film compound (3) was obtained.

It is 56 % when the gel fraction of the obtained film compound (3) is investigated.

It became a film compound (1) and the low value was shown.

This is meaning that there are polymerizable unsaturated groups contained in one molecule as for more acrylic polymers (1) compared with an acrylic polymer (3).

[0056]

[ADVANTAGE of the Invention] The acrylic polymer which has the polymerizable unsaturated group of this invention at the molecule terminal does not have conventionally well-known initiator residues, such as a solvent compound residue, and an azo group, a peroxide group, in the molecule terminal excluding an emulsifier or a dispersing agent, and the polymerizable unsaturated group is reliably transduced into the molecule terminal.



[0057] Moreover, the acrylic polymer which has the polymerizable unsaturated group of this invention at the molecule terminal is a thing which is acquired as a solventless and viscous liquid and which carry out prepolymer use, when introducing a polymerizable unsaturated group into the prepolymer, in order that there may be no need of not necessarily carrying out solvent elimination, the molecule terminal serves as a fully controlled polymer.